Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supporting Information:

Supramolecular polymerization of oligopyrenotides - stereochemical control by single, natural nucleotides

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General procedures

The required pyrene building block[1] and the oligomers were synthesized and purified according to a published procedures.[2]

Spectroscopic methods

Unless otherwise indicated, all experiments were performed in sodium phosphate buffer (10 mM, 1M NaCl, pH 7.0) for 5 µM oligomer concentration, ε_{350}= 20'000 $dm^3 \times mole^{-1} \times cm^{-1}$ was used for pyrene units.

Temperature dependent UV/VIS spectra were collected with an optic path of 1 cm over the range of 200-500 nm at 10-90 ºC with a 10 ºC interval on *Varian Cary-100 Bio*-UV/VIS spectrophotometer equipped with a *Varian Cary*-block temperature controller. The cell compartment was flushed with N_2.

Thermal melting experiments were carried out on *Varian Cary-100 Bio*-UV/VIS spectrophotometer equipped with a *Varian Cary*-block temperature controller and data were collected with Varian WinUV software at 354 nm (cooling-ramp in the temperature range of 10-90°C, temperature gradient of 0.5°C/min). Data are normalized at maximum of absorbance (at high temperature).

Temperature dependent fluorescence data were collected on a *Varian Cary Eclipse* fluorescence spectrophotometer equipped with a *Varian Cary*-block temperature controller (excitation at 350 nm; excitation and emission slit width of 2.5 nm) using 1 cm x 1 cm quartz cuvettes. *Varian Eclipse* software was used to investigate the fluorescence of the oligopyrenes at a wavelength range of 370-700 nm in the temperature range of 10-90 °C.

CD spectra were recorded on a *JASCO J-715* spectrophotometer using quartz cuvettes with an optical path of 1 cm. (Scanning speed: 100 nm/min; data pitch: 0.5 nm; band width: 1.0 nm; response: 1 sec).

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[1] Langenegger, S. M.; Häner, R. *ChemBioChem* **2005**, *6*, 848-851.
[2] Nussbaumer, A. L.; Studer, D.; Malinovskii, V. L.; Häner, R. *Angew. Chem. Int. Ed.* **2011**, *50*, 5490-5494.

The calculation of the g-factor was done with the equation G = CD(mdeg)/(32980*Abs) using the absorbance and CD values in mdeg recorded by the *JASCO-J-715*.

Amplification experiment using 10% chiral information. Oligomer **1** (5 µM building block concentration) was mixed together with phosphate buffer and sodium chloride and heated to 90°C (10 mM, 1M NaCl, pH 7.0). After cooling and equilibration of 1 week, 10% (0.5 µM building block concentration) of the corresponding oligomers of **3**, **5**, **7** and **11** were added to the preformed supramolecular polymers. From then on data points were taken after 2 hours, 1 day, 4 days and then every week until one month was passed.

Mass spectrometry of oligomers was performed with a Sciex QSTAR pulsar (hybrid quadrupole time-of-flight mass spectrometer, *Applied Biosystems*). ESI-TOF MS (negative mode, CH_3CN/H_2O/TEA) data of compounds are presented in Table 1. LC-MS was performed with a Shimadzu LCMS-2010EV high-performance liquid chromatograph/ mass spectrometer.

Table 1. Mass spectrometry data of synthesized oligomers (ESI-TOF MS, negative mode, CH_3CN/H_2O/TEA).

	Oligonucleotide	**Molecular Formula**	**Calc. average mass**	**Found mass**
1	SSS SSS S	$C_{168}H_{156}N_{14}O_{40}P_6$	3203.0	3203.0
2	(5') SS SSS SSC	$C_{177}H_{167}N_{17}O_{46}P_7$	3492.0	3492.0
3	(5') CSS SSS SS	$C_{177}H_{167}N_{17}O_{46}P_7$	3492.0	3490.5
4	(5') CSS SSS SSC	$C_{186}H_{178}N_{20}O_{52}P_8$	3781.4	3782.0
5	(5') SS SSS SSG	$C_{178}H_{167}N_{19}O_{46}P_7$	3532.2	3531.0
6	(5') GSS SSS SS	$C_{178}H_{167}N_{19}O_{46}P_7$	3532.2	3531.0
7	(5') GSS SSS SSG	$C_{188}H_{178}N_{24}O_{52}P_8$	3861.4	3863.0
8	(5') SS SSS SST	$C_{178}H_{168}N_{16}O_{47}P_7$	3507.2	3507.0
9	(5') TSS SSS SS	$C_{178}H_{168}N_{16}O_{47}P_7$	3507.2	3505.5
10	(5') TSS SSS SST	$C_{188}H_{180}N_{18}O_{54}P_8$	3811.4	3811.0
11	(5') SS SSS SSA	$C_{178}H_{167}N_{19}O_{45}P_7$	3516.2	3516.0
12	(5') ASS SSS SS	$C_{178}H_{167}N_{19}O_{45}P_7$	3516.2	3515.5
13	(5') ASS SSS SSA	$C_{188}H_{178}N_{24}O_{50}P_8$	3829.4	3830.0

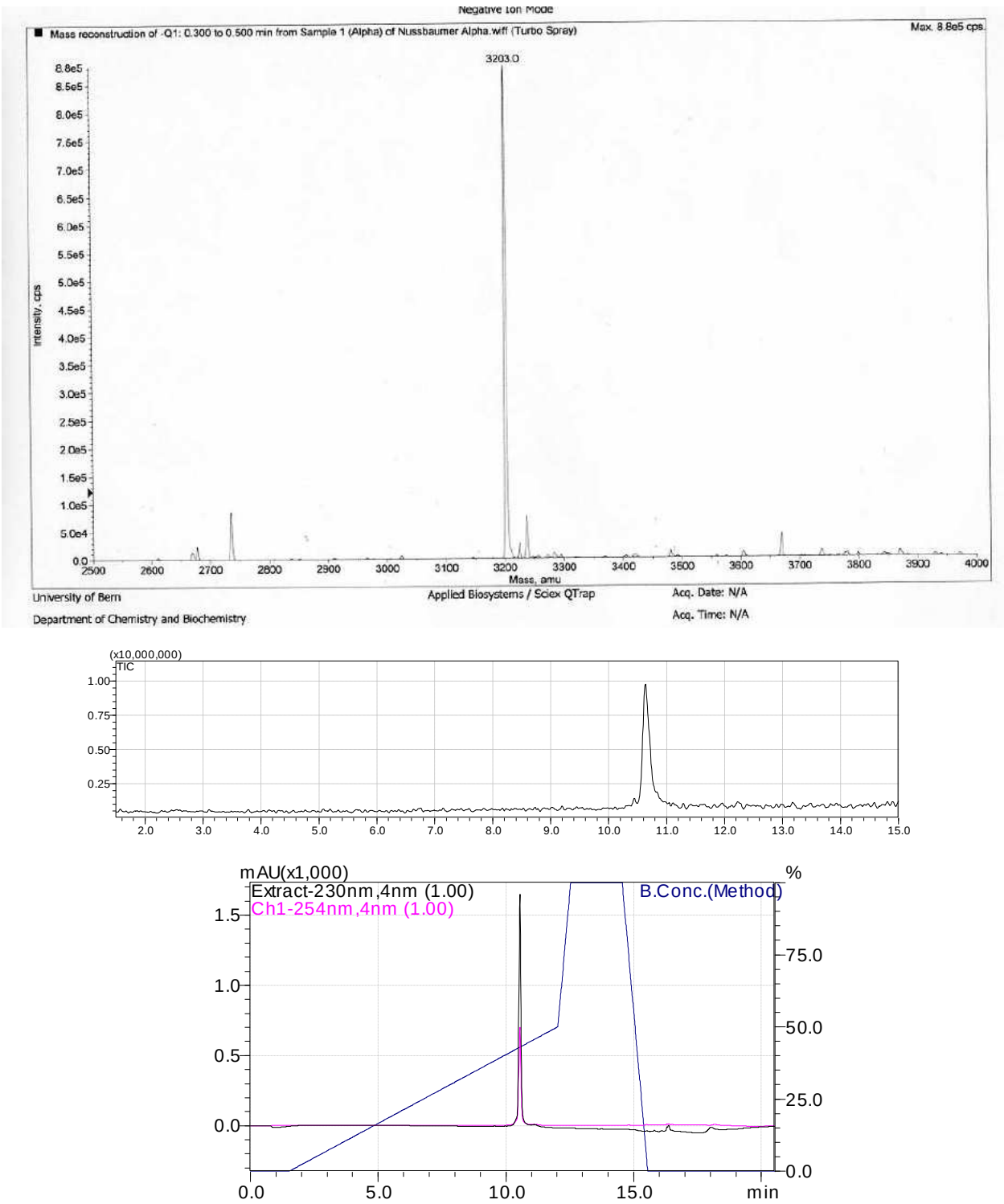

Figure 1. MS and LC-MS data of oligomer **Py_7 (1)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 230 nm and 254 nm**.**

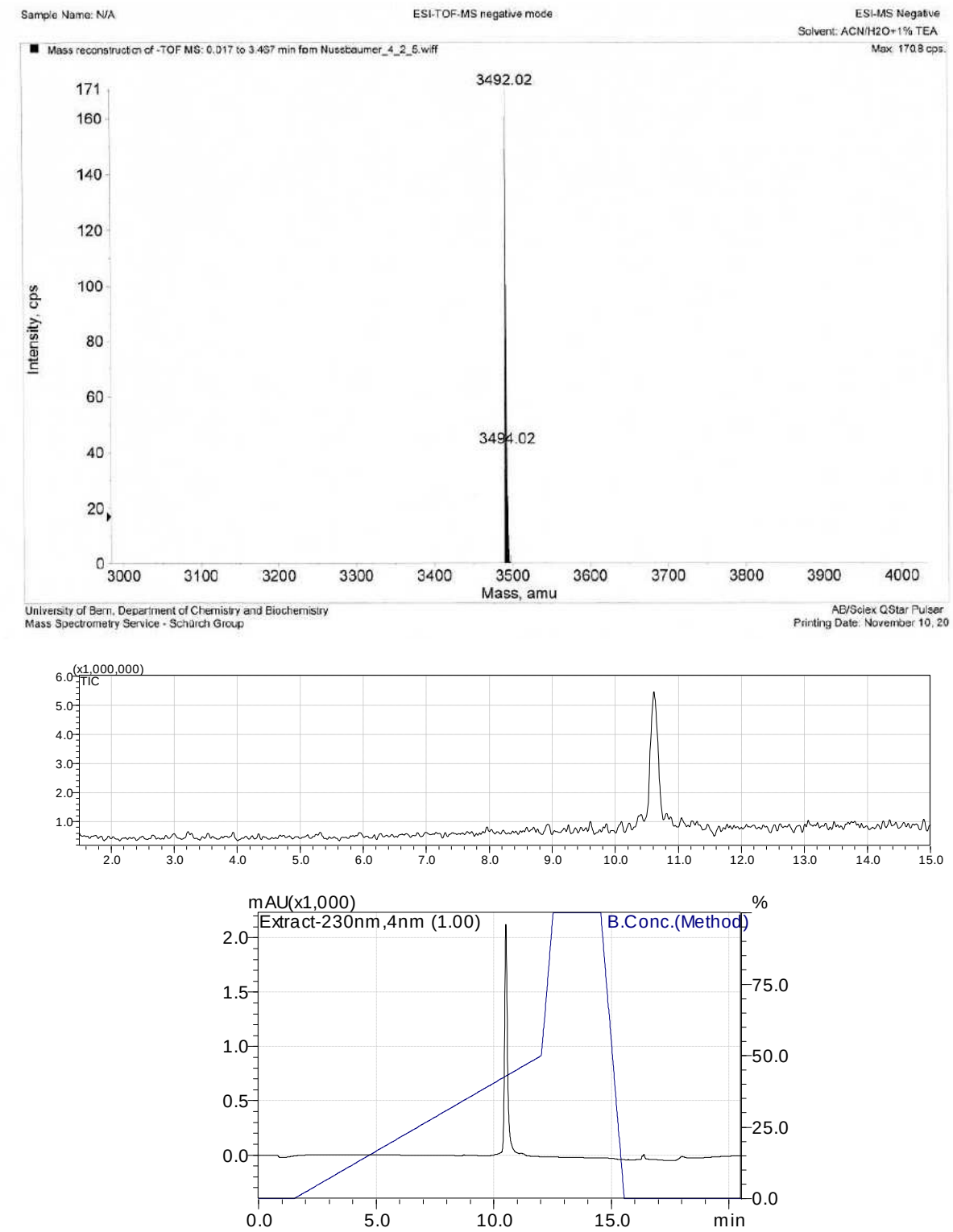

Figure 2. MS and LC-MS data of oligomer **Py_7-C (2)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 230 nm**.**

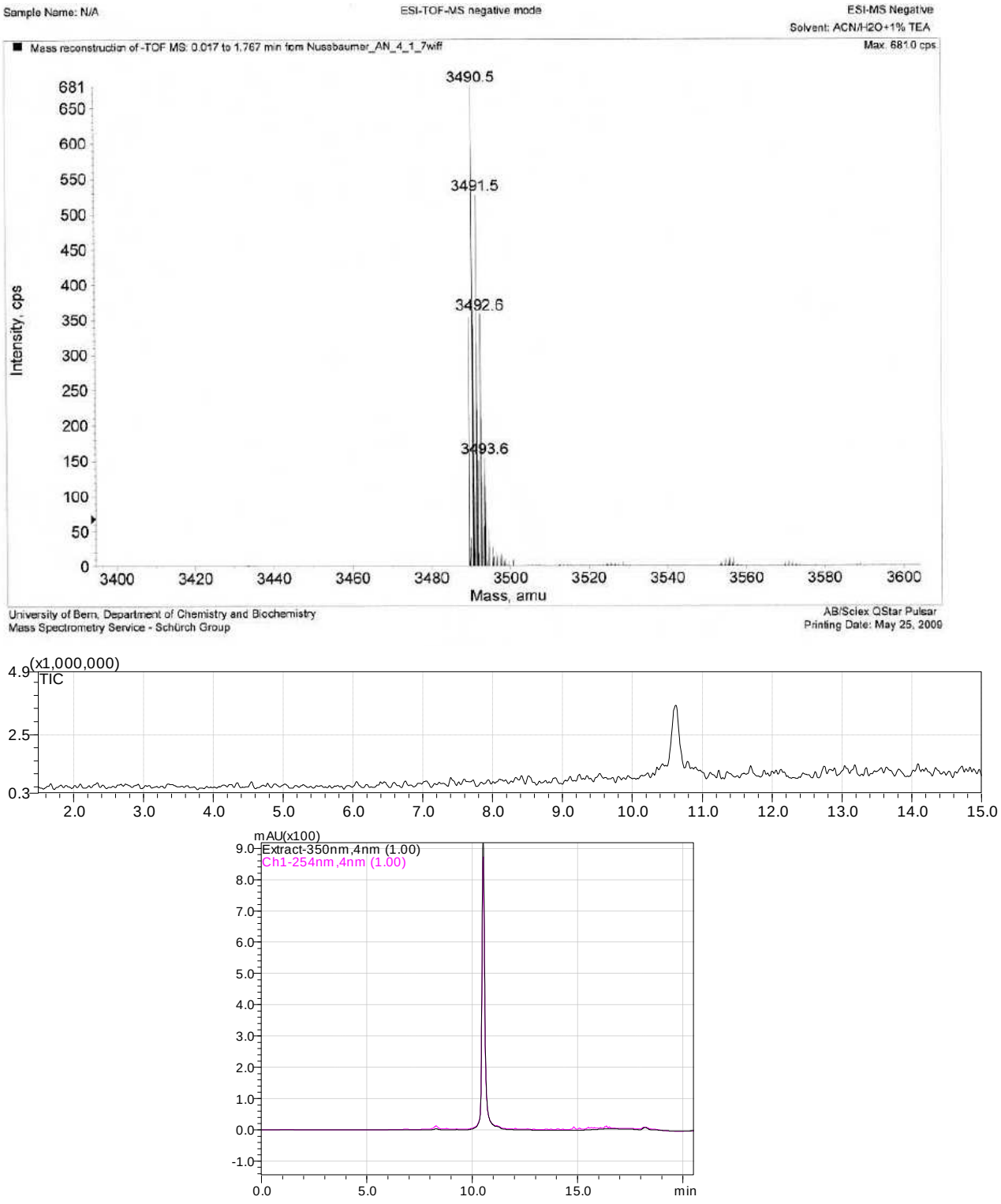

Figure 3. MS and LC-MS data of oligomer **C-Py$_7$ (3)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm **.**

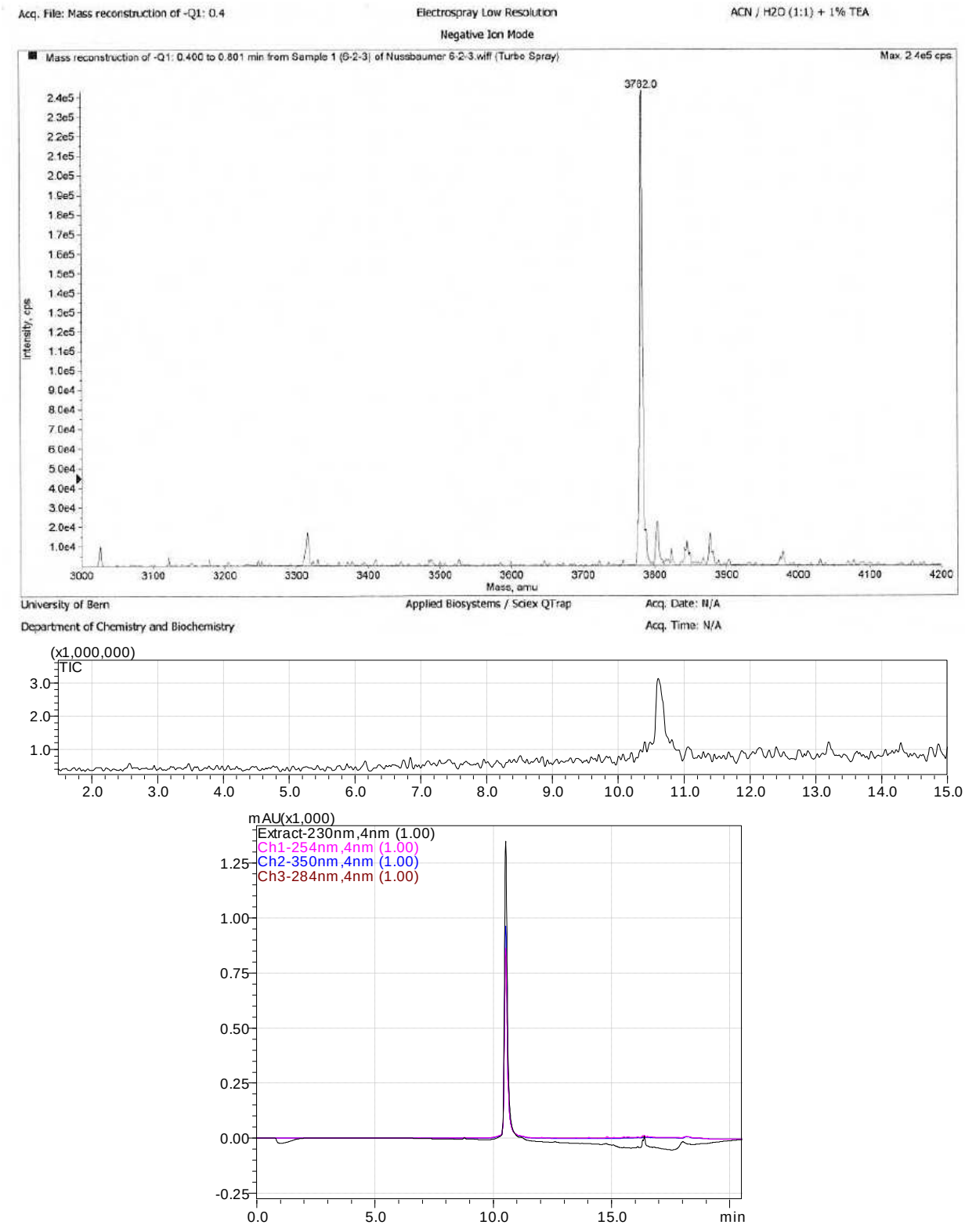

Figure 4. MS and LC-MS data of oligomer **C-Py$_7$-C (4)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 230 nm, 254 nm, 284 nm and 350 nm **.**

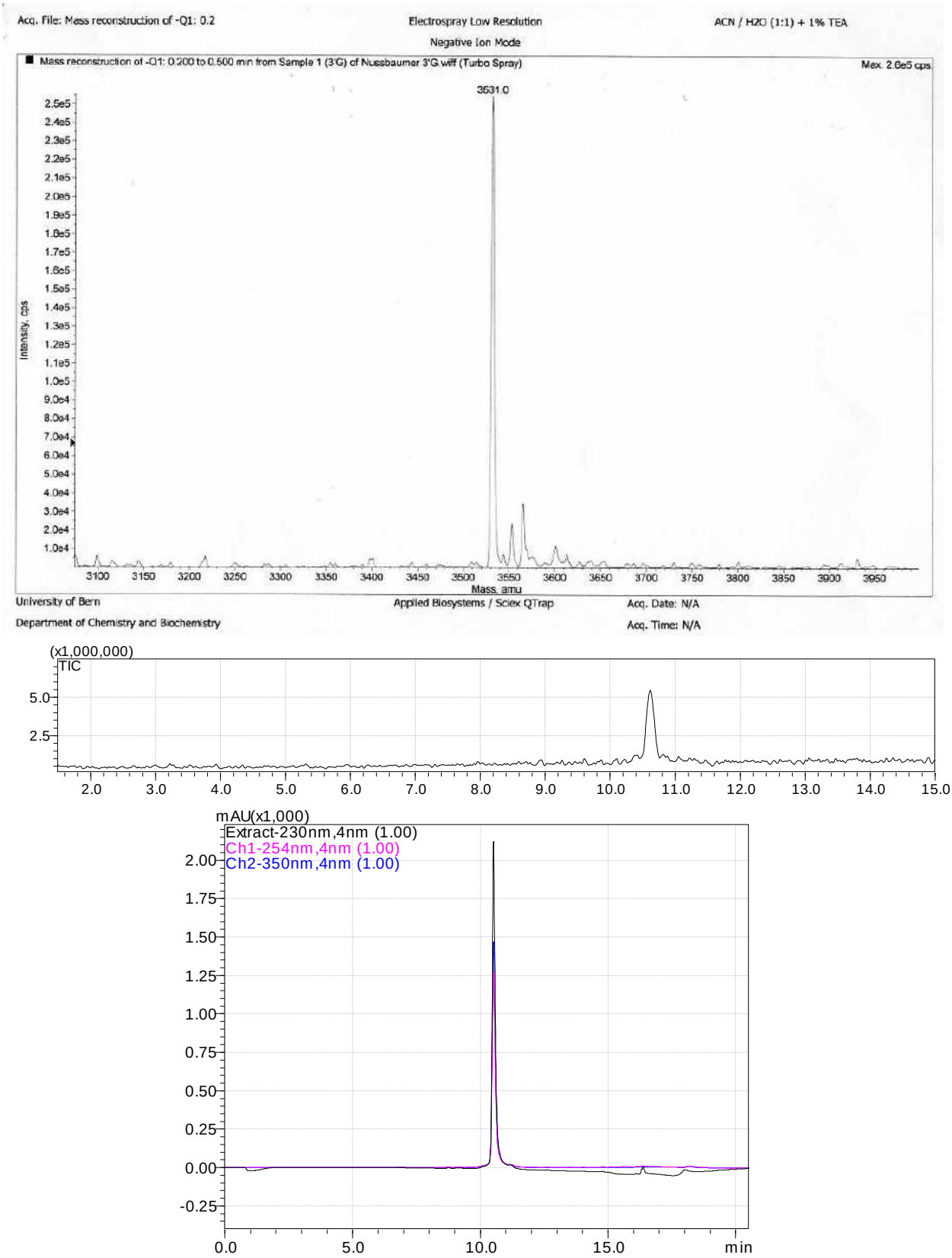

Figure 5. MS and LC-MS data of oligomer **Py_7-G (5)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 230 nm, 254 nm and 350 nm **.**

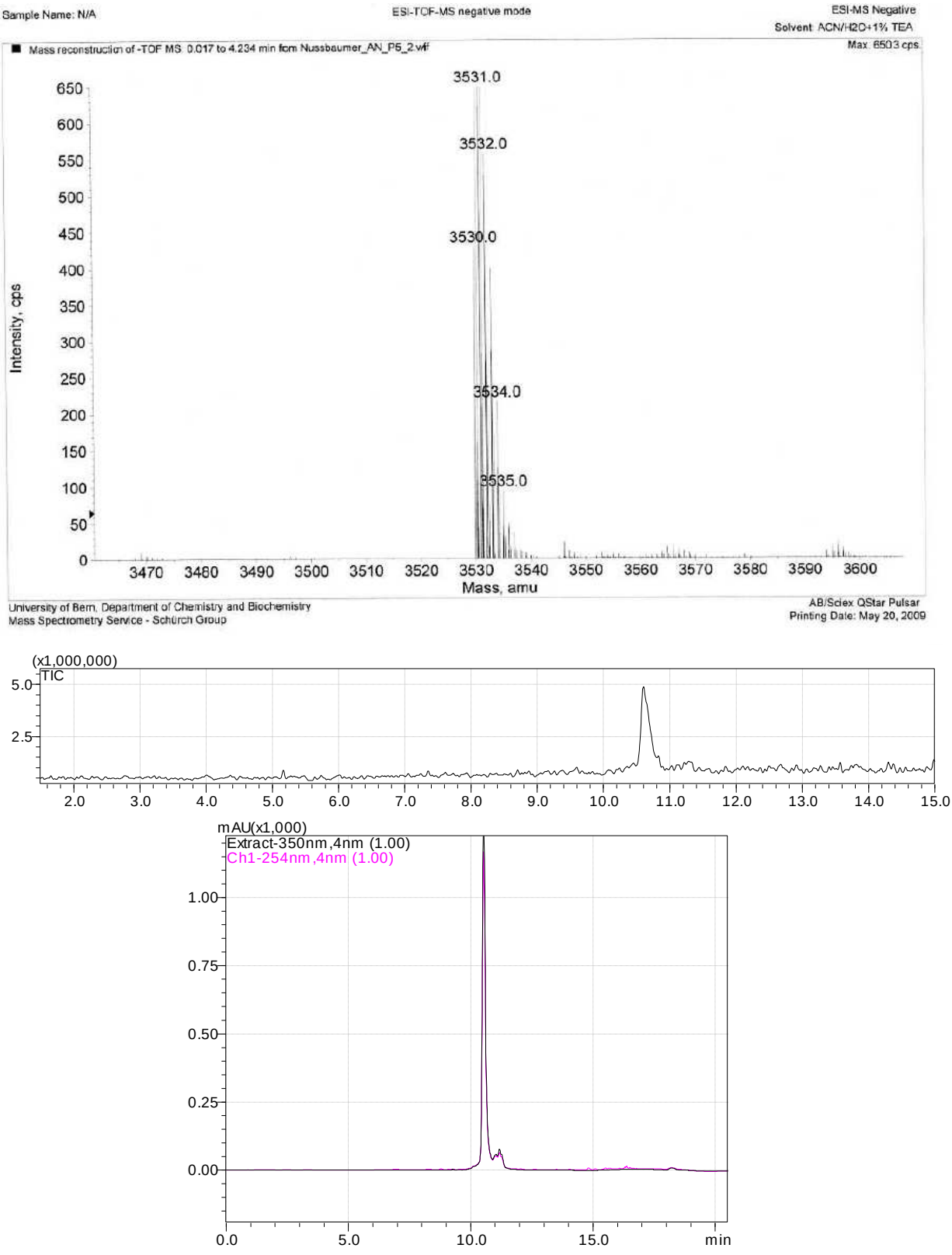

Figure 6. MS and LC-MS data of oligomer **G-Py$_7$ (6)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm.

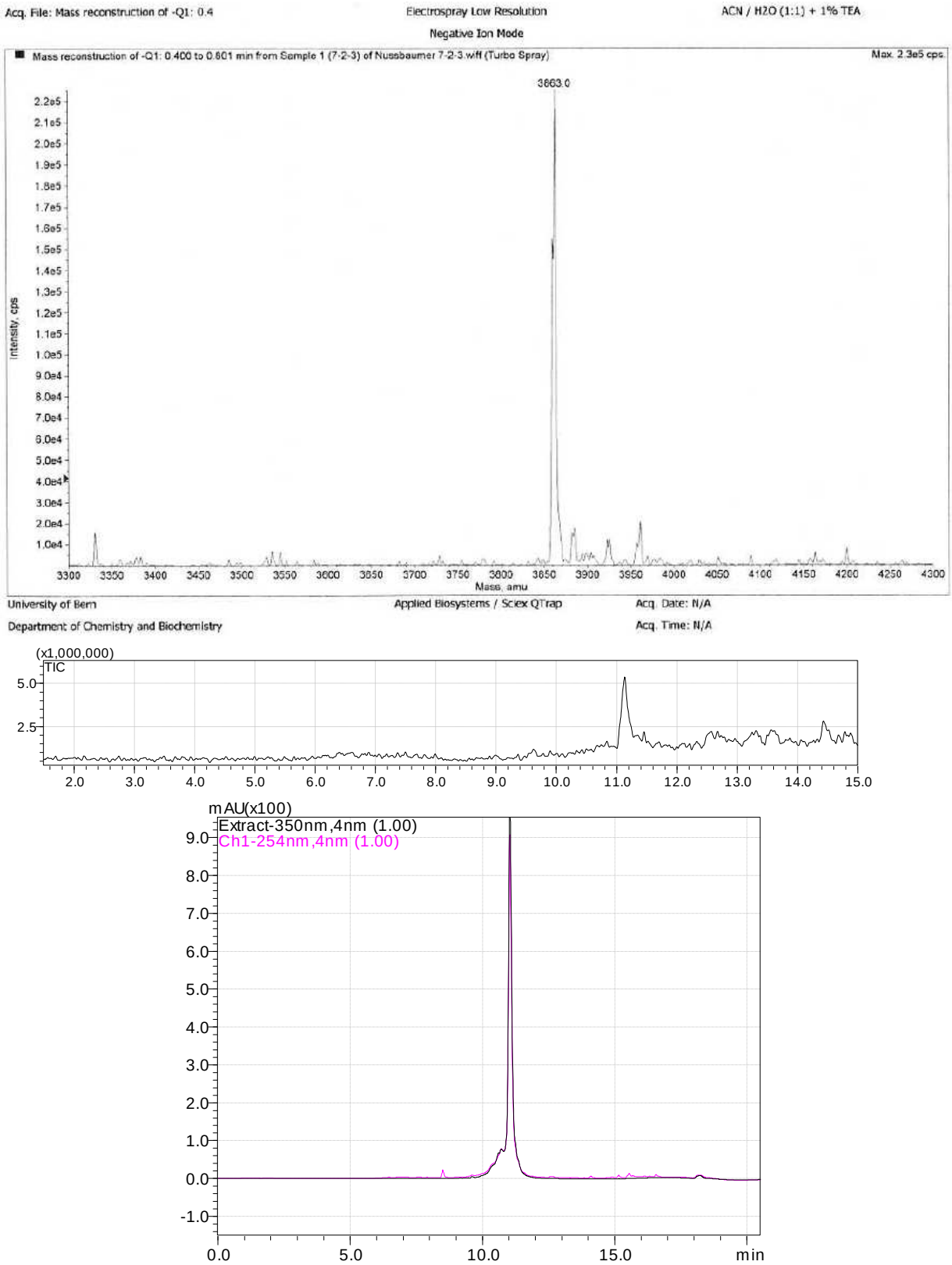

Figure 7. MS and LC-MS data of oligomer **G-Py$_7$-G (7)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm **.**

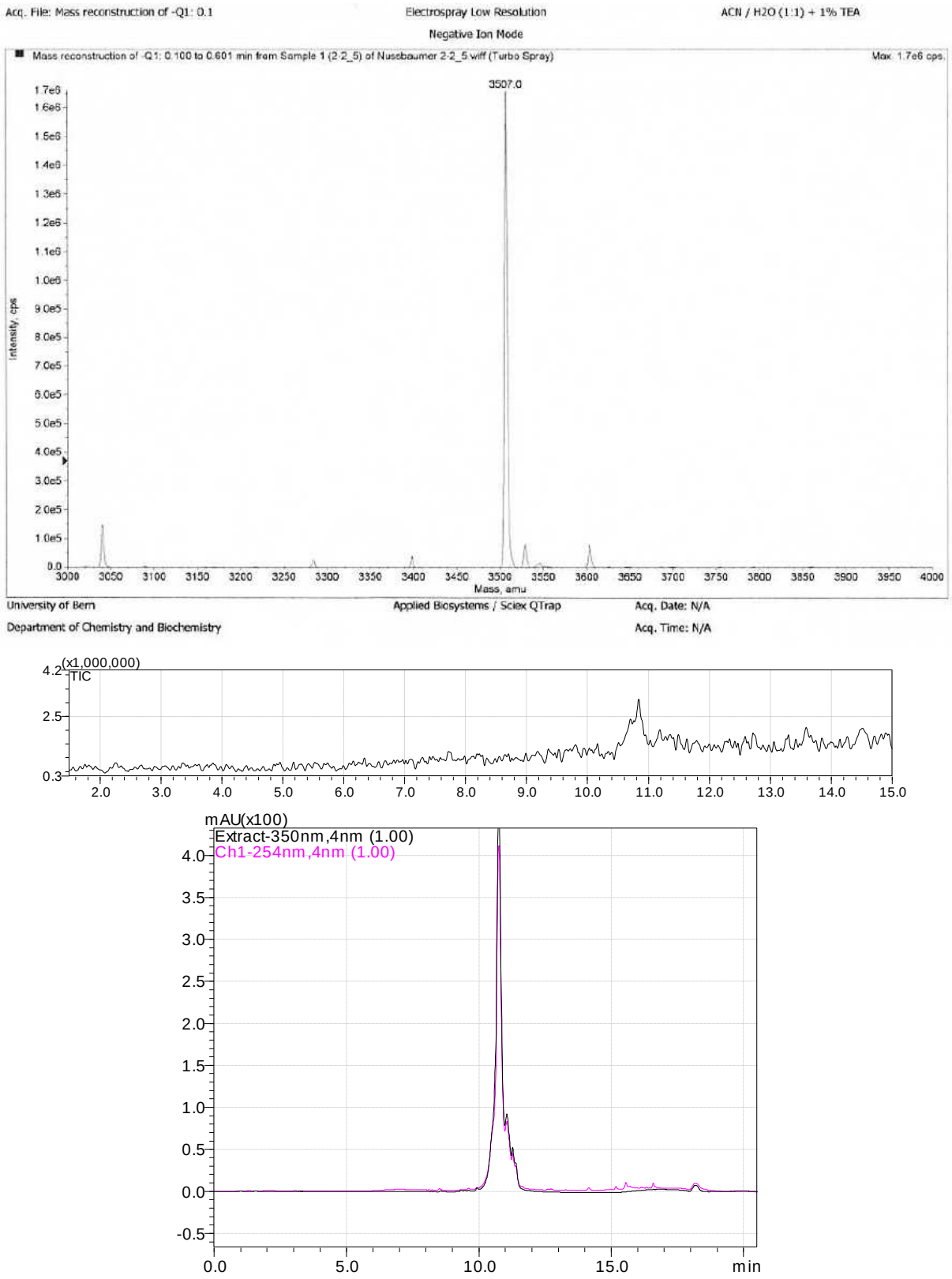

Figure 8. MS and LC-MS data of oligomer **Py_7-T (8)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm .

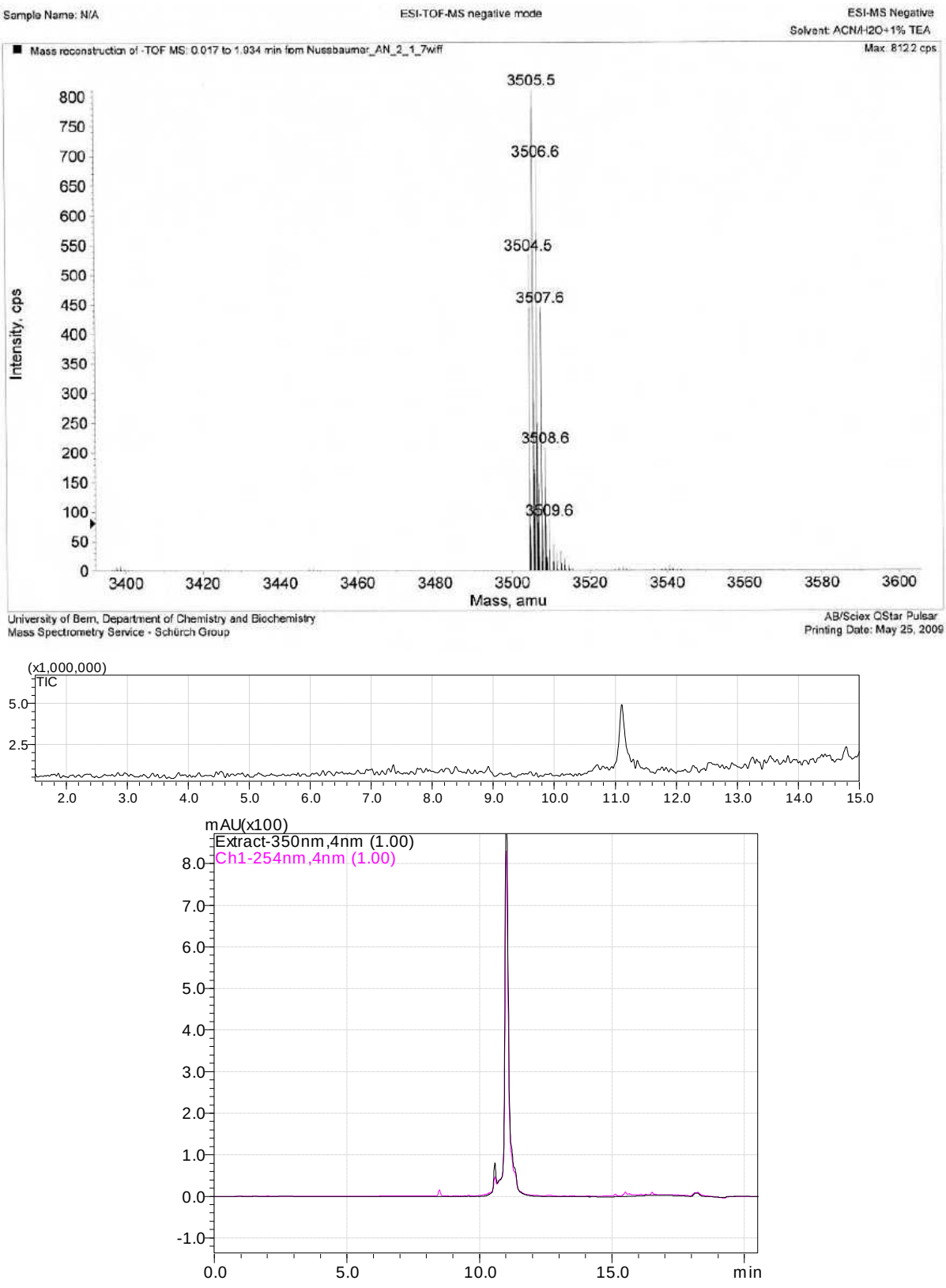

Figure 9. MS and LC-MS data of oligomer **T-Py$_7$ (9)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm **.**

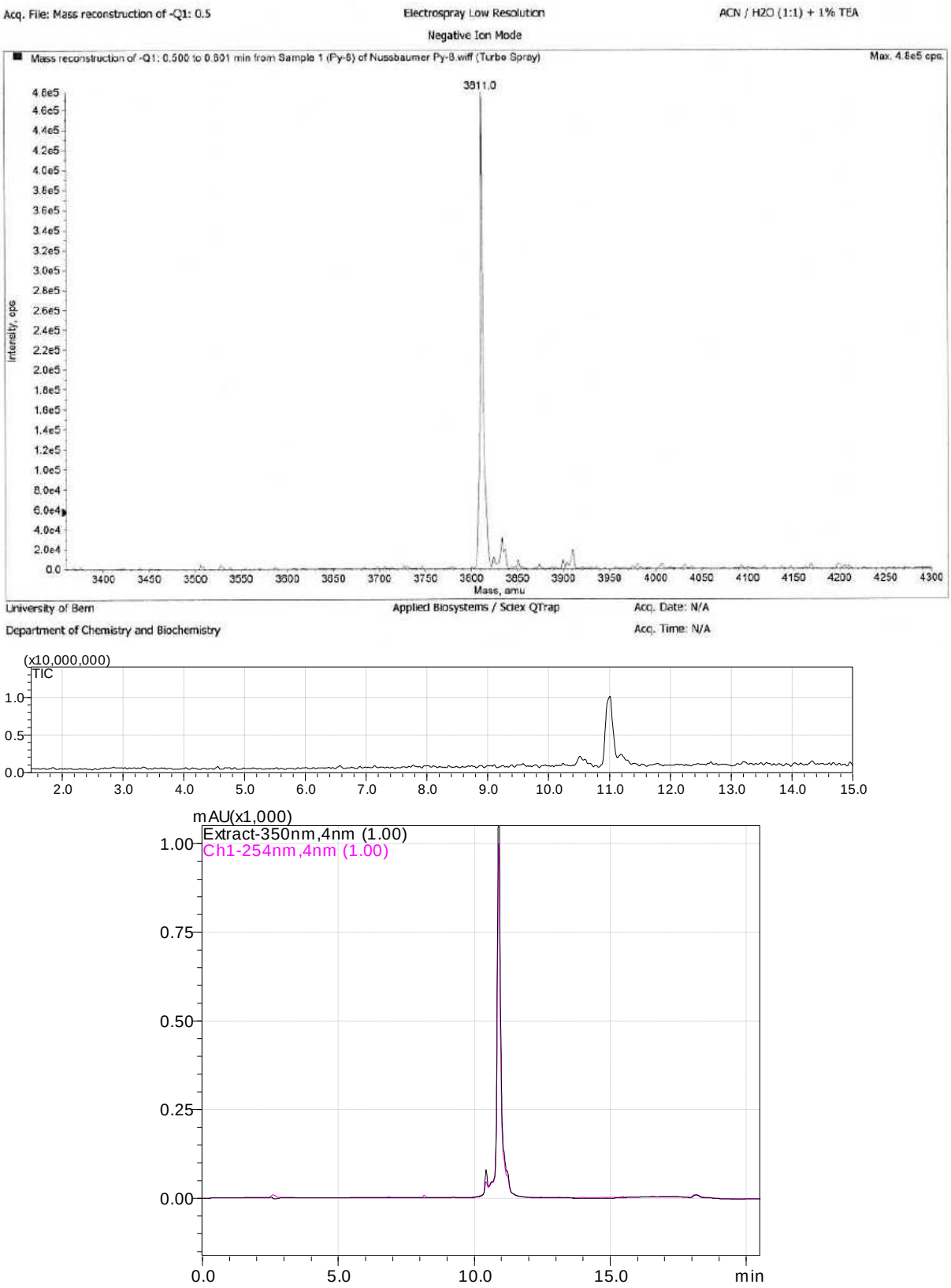

Figure 10. MS and LC-MS data of oligomer **T-Py$_7$-T (10)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm.

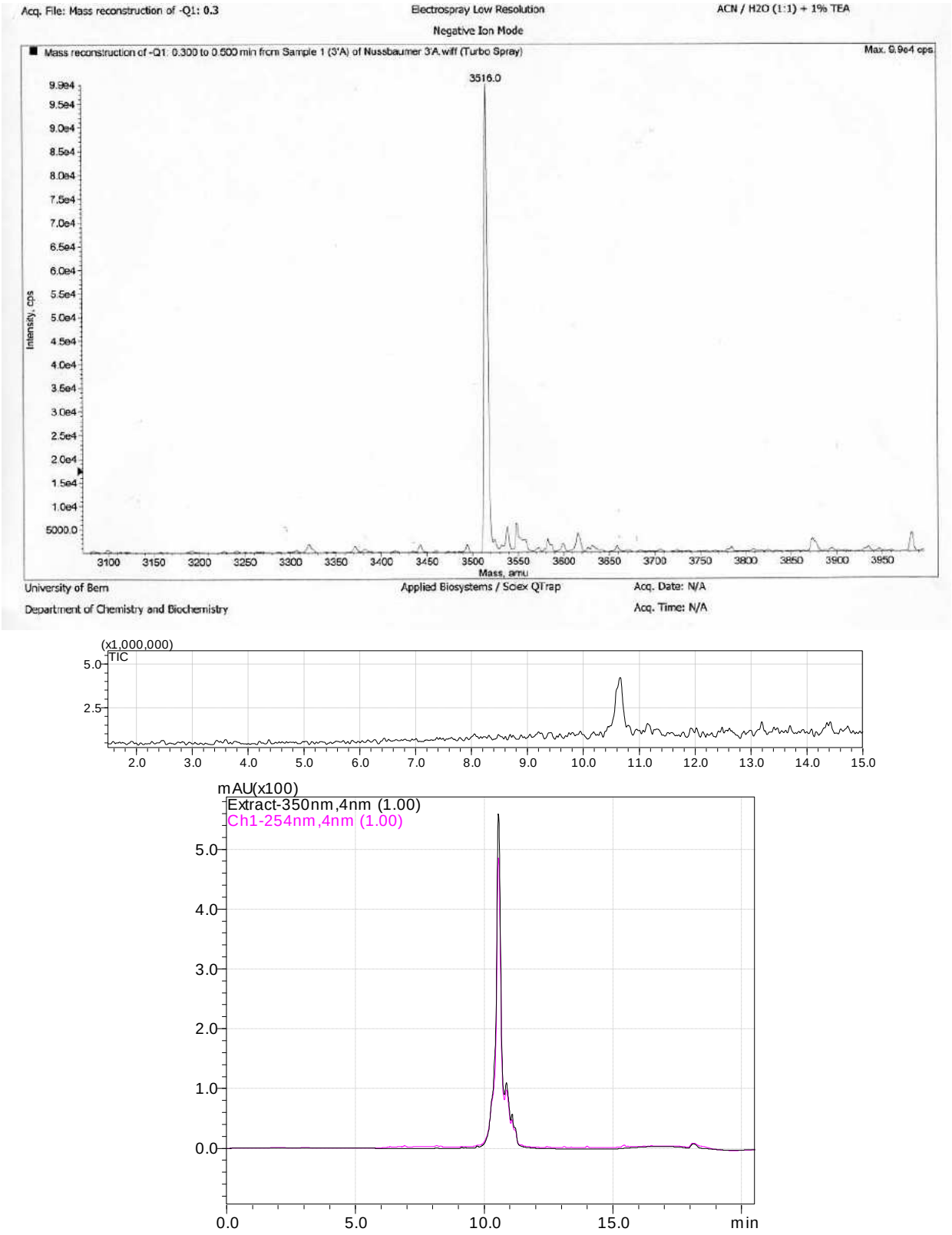

Figure 11. MS and LC-MS data of oligomer **Py_7-A (11)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm **.**

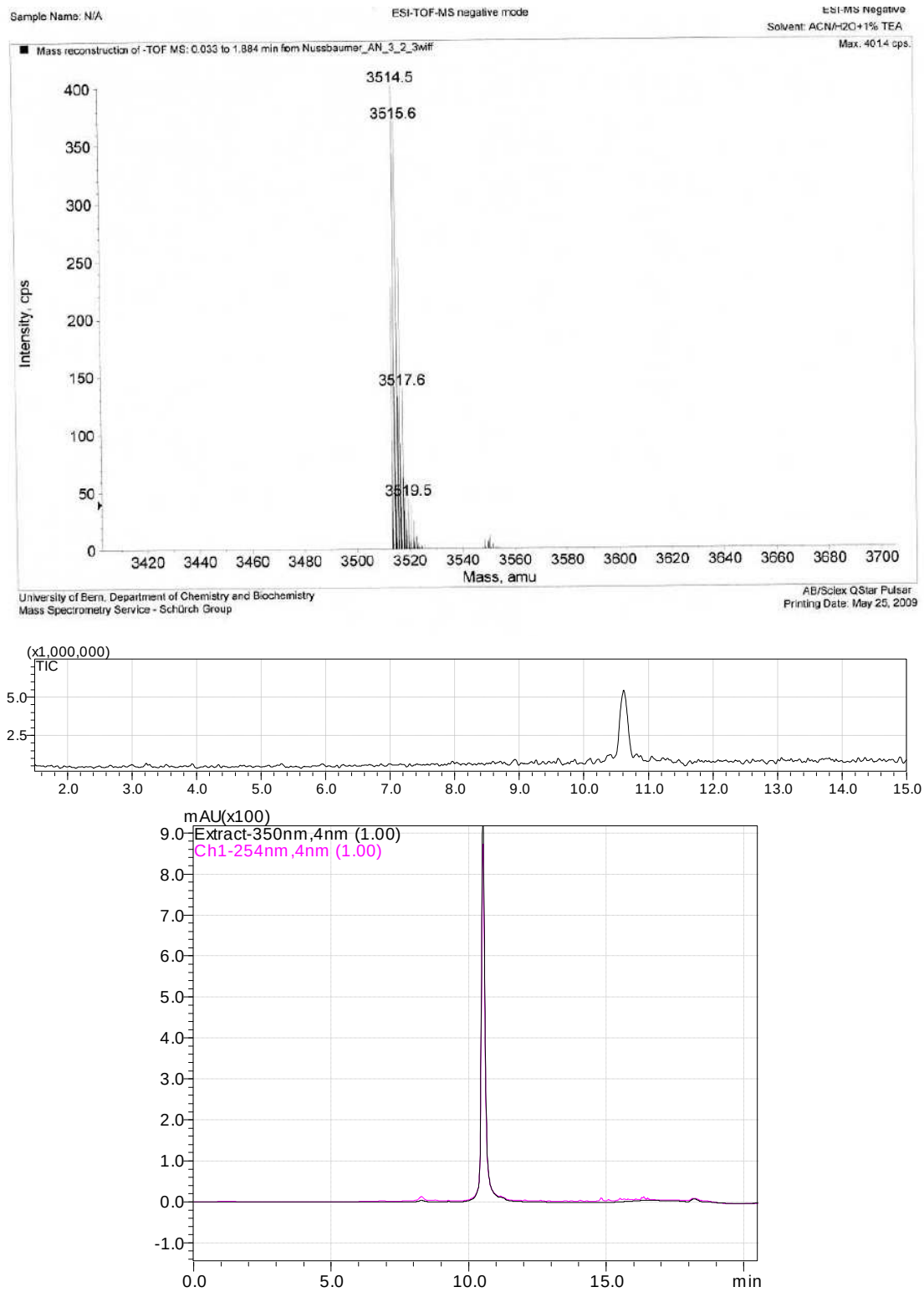

Figure 12. MS and LC-MS data of oligomer **A-Py$_7$ (12)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm.

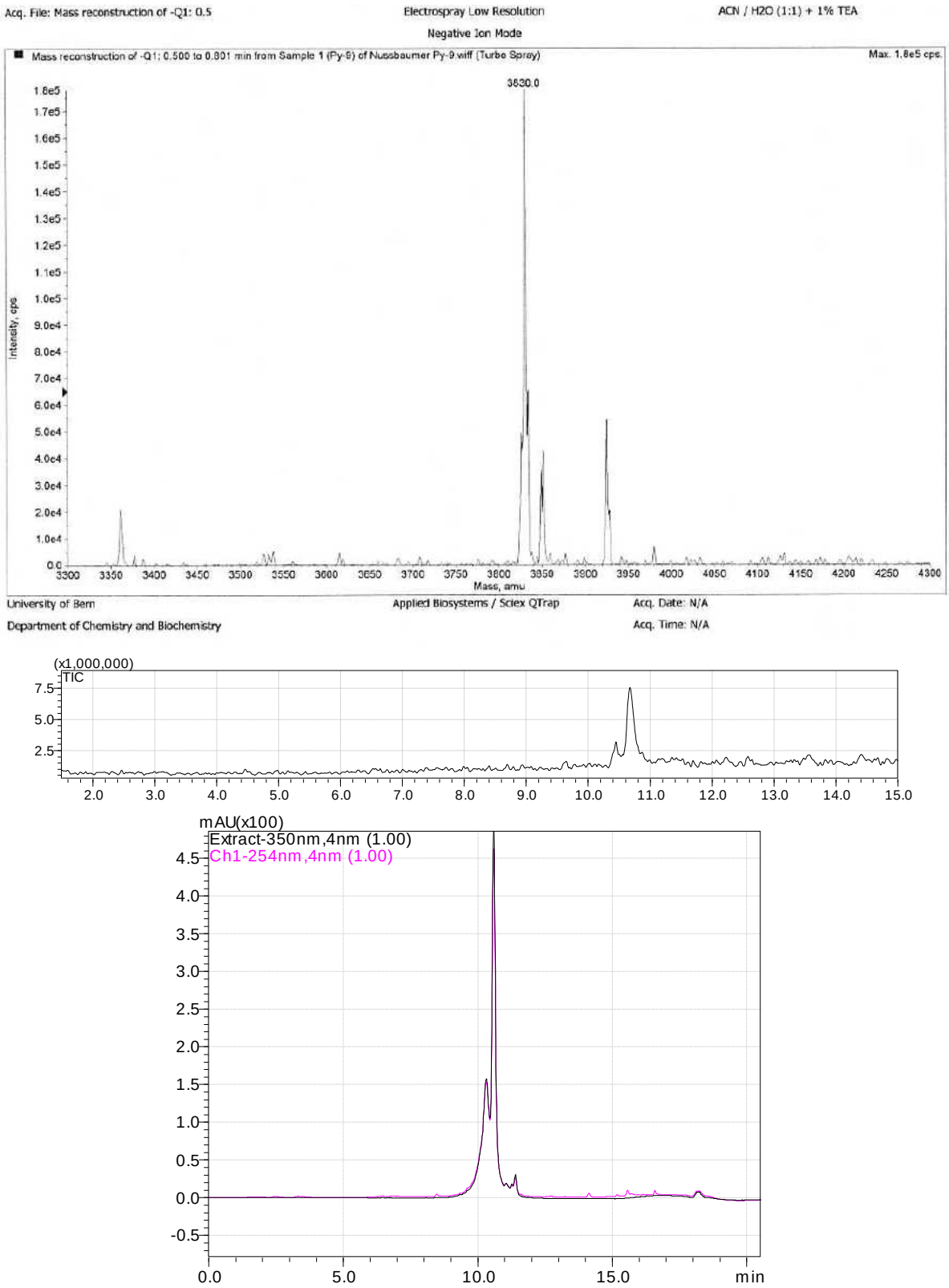

Figure 13. MS and LC-MS data of oligomer **A-Py$_7$–A (13)**; MS-spectra (top) total ion chromatogram (middle) and chromatogram using detection wavelength at 254 nm and 350 nm **.**

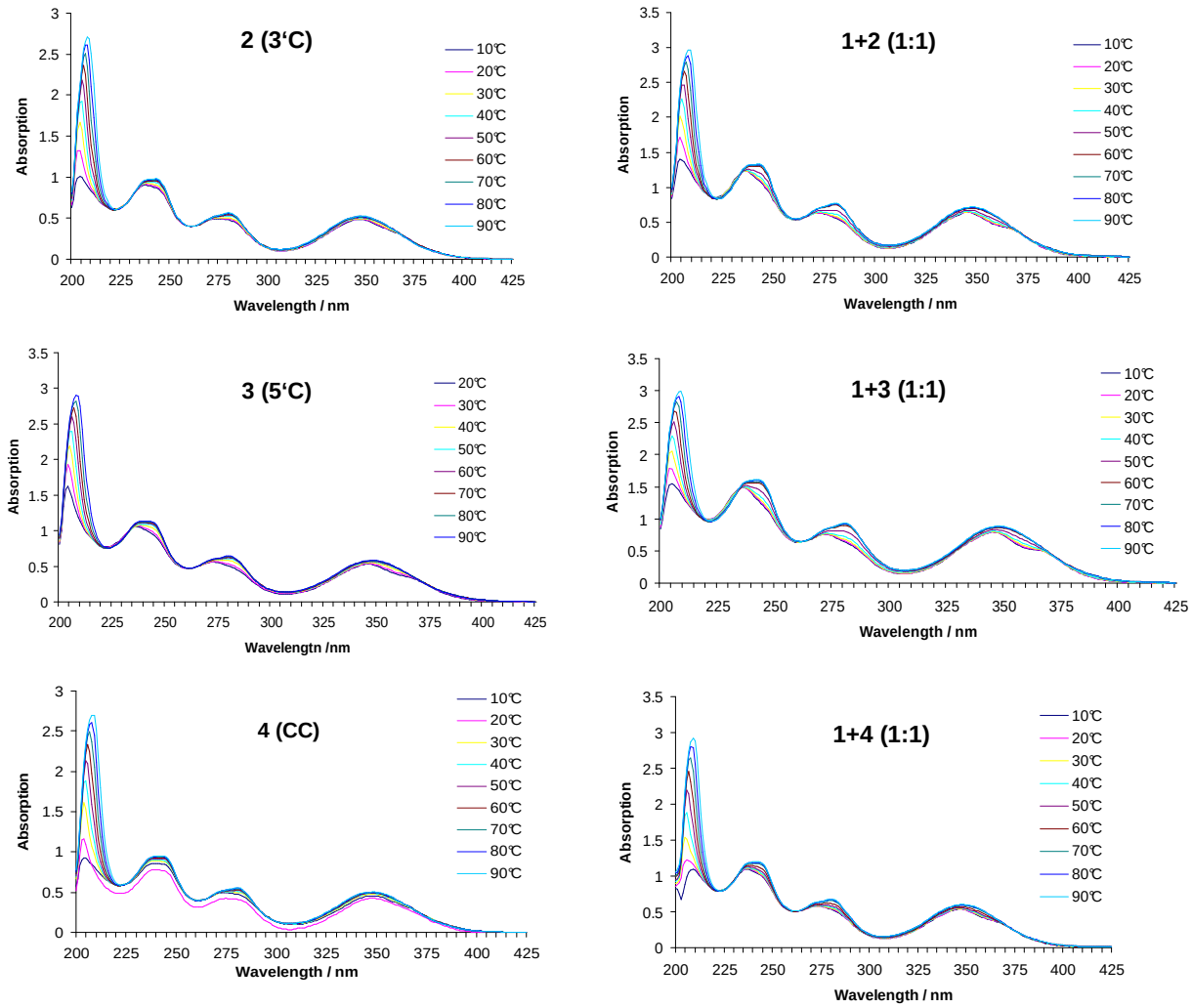

Figure 14. Temperature variable absorbance spectra of oligomer **2, 3, 4** (left) and co-aggregates **1*2**, **1*3**, **1*4** in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.

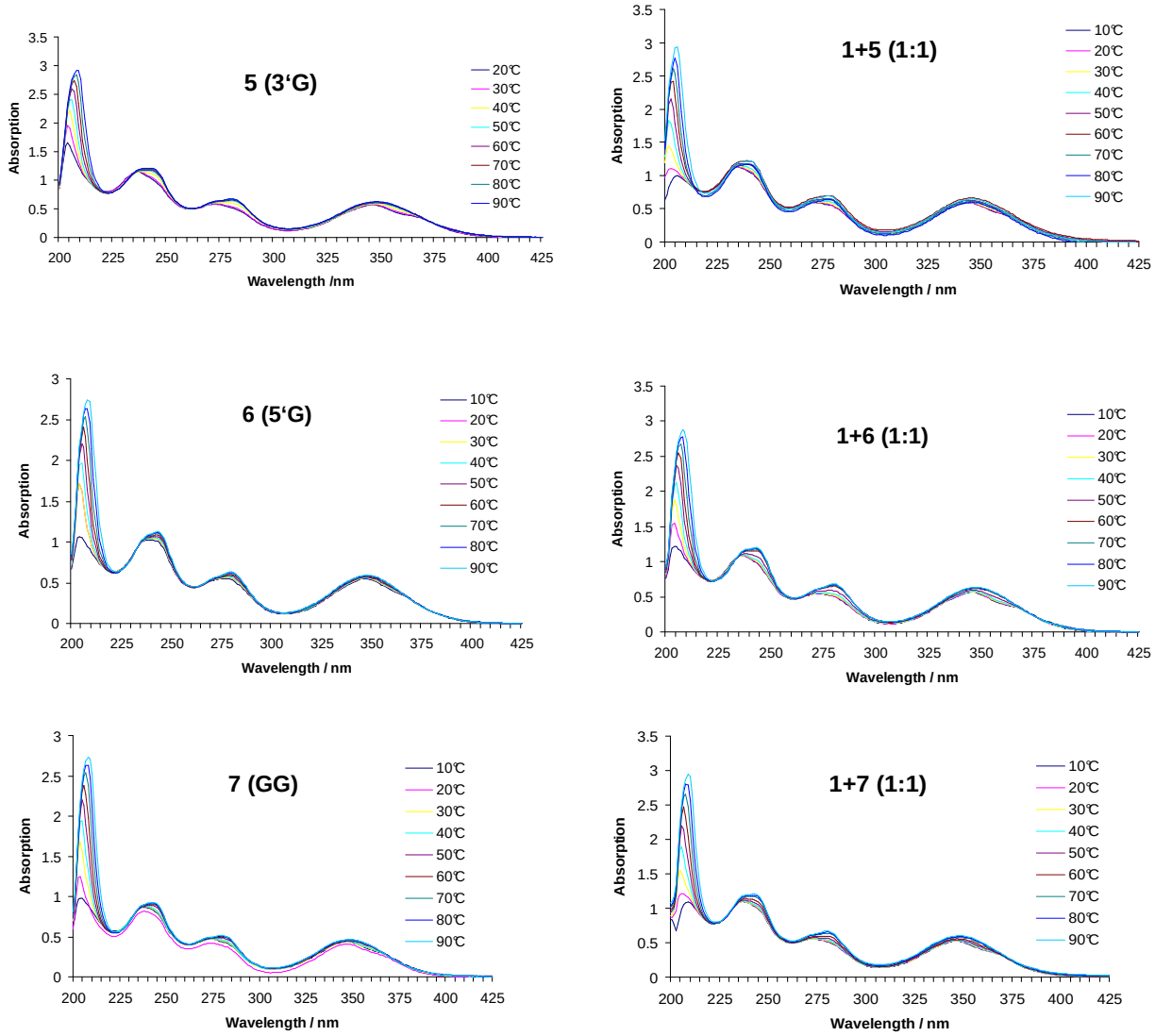

Figure 15. Temperature variable absorbance spectra of oligomer **5, 6, 7** (left) and co-aggregates **1*5**, **1*6**, **1*7** in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.

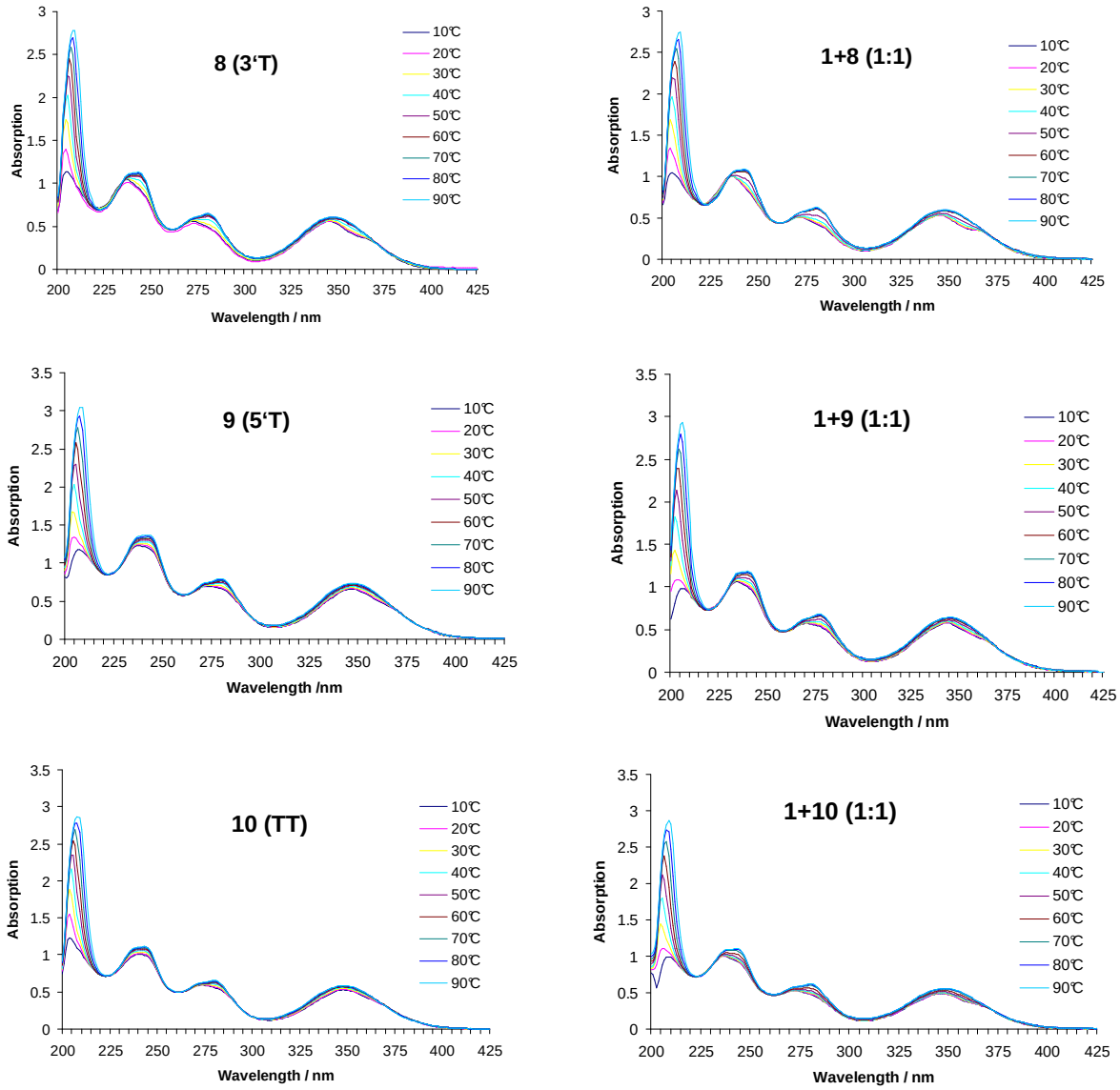

Figure 16. Temperature variable absorbance spectra of oligomer **8, 9, 10** (left) co-aggregates **1*8**, **1*9**, **1*10** in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.

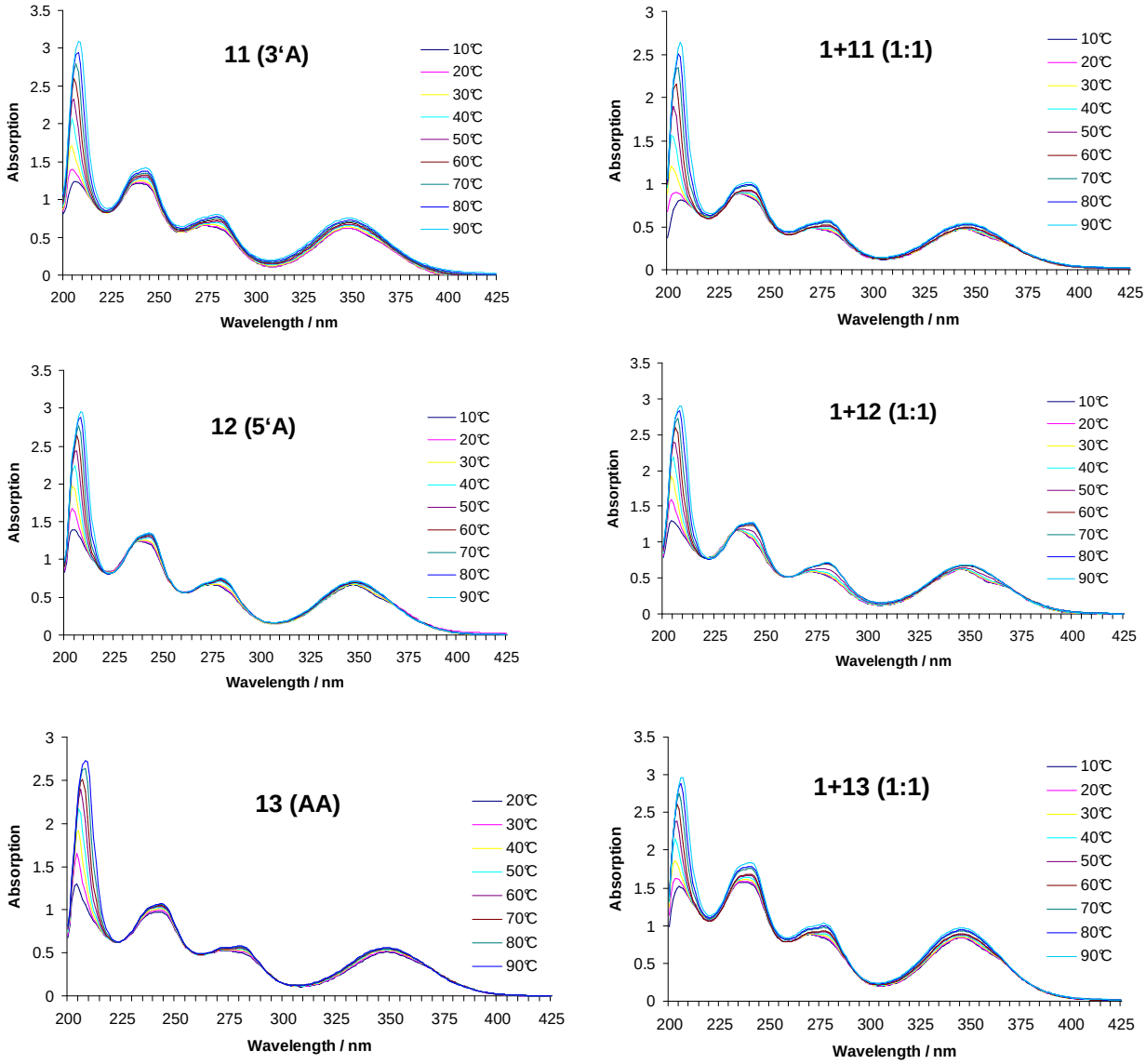

Figure 17. Temperature variable absorbance spectra of oligomer **11, 12, 13** (left) and co-aggregates **1*11**, **1*12**, **1*13** in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.

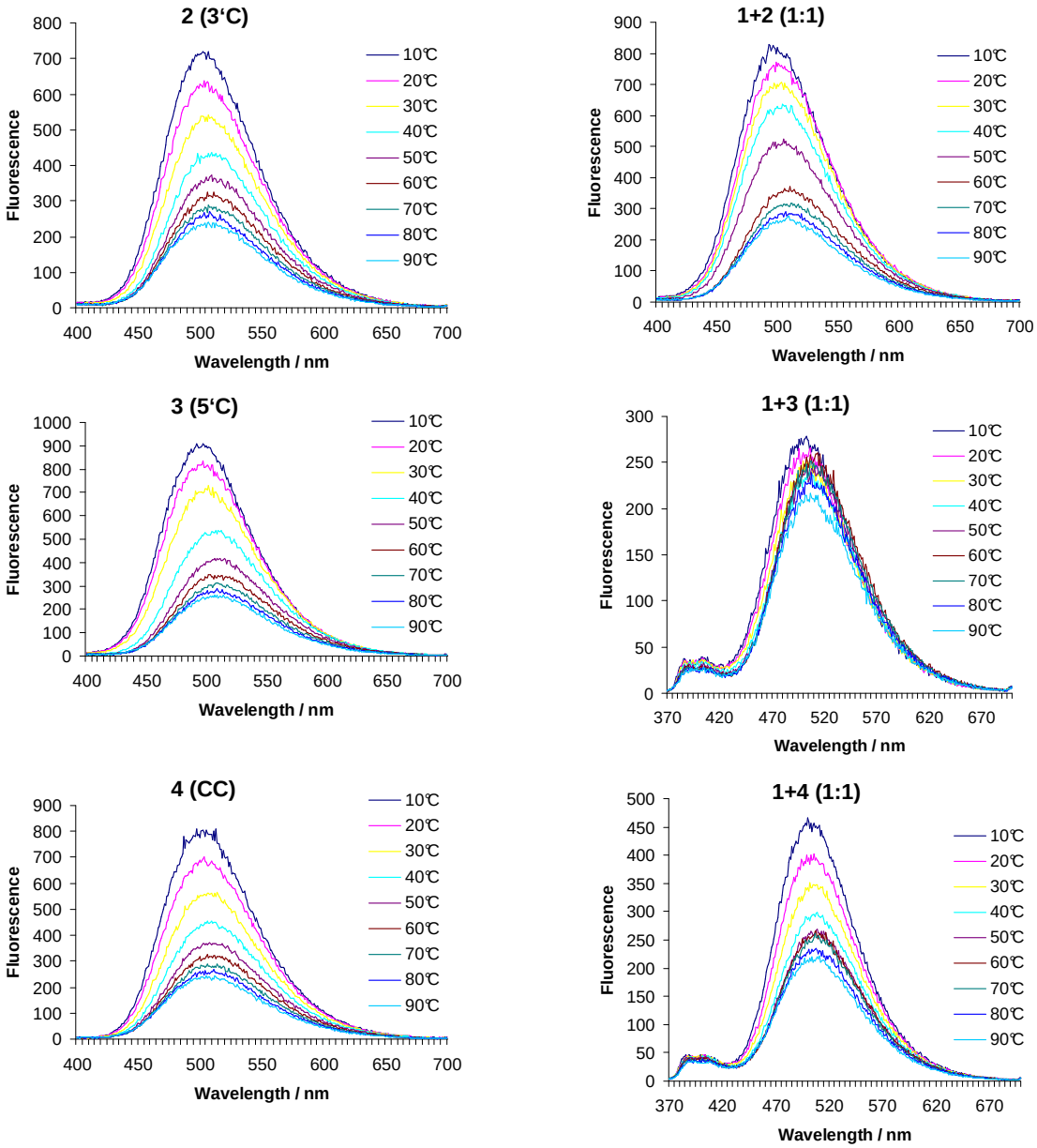

Figure 18. Temperature variable fluorescence spectra of oligomer **2, 3, 4** (left) and co-aggregates **1*2**, **1*3**, **1*4** in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 μM.

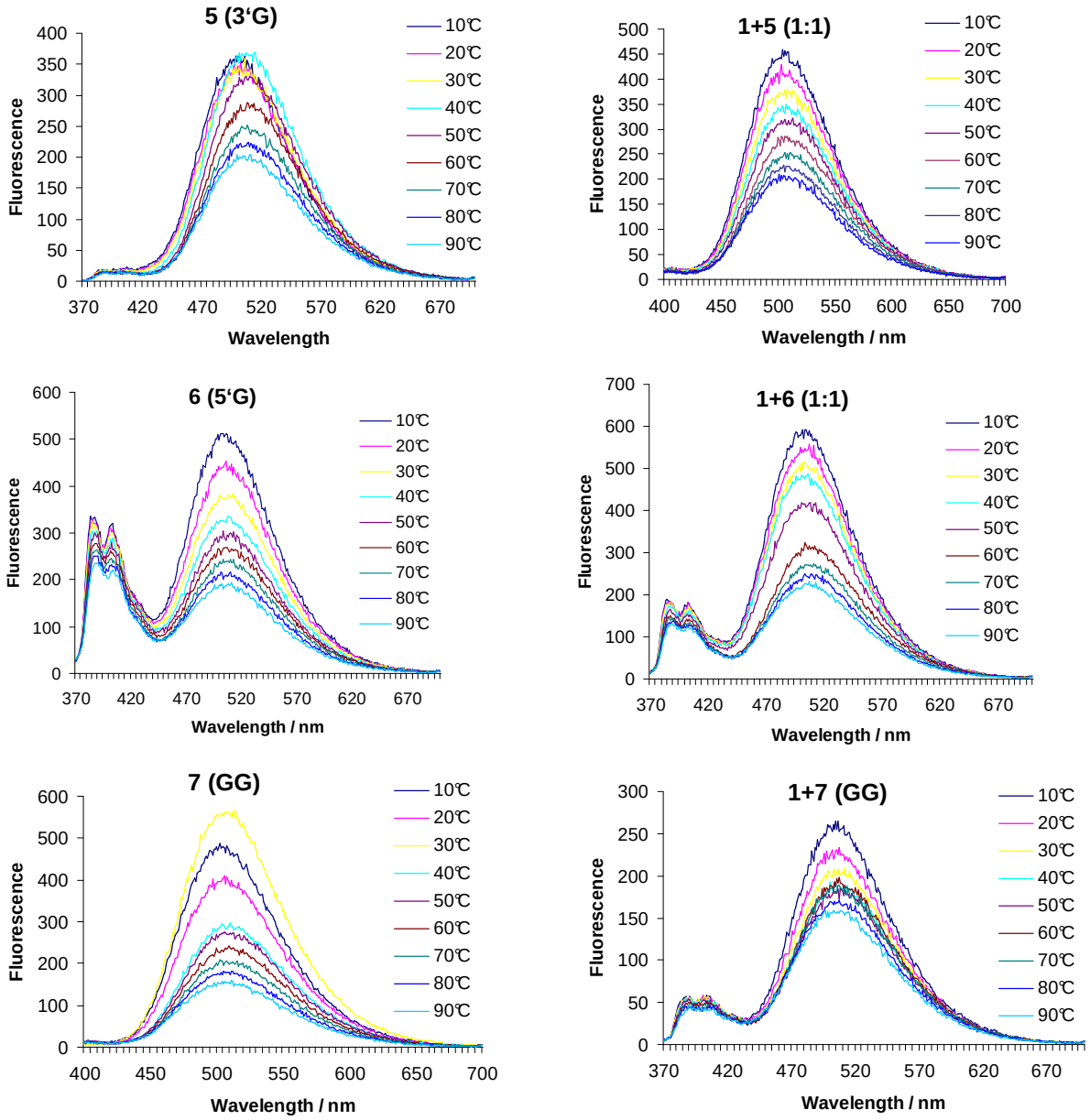

Figure 19. Temperature variable fluorescence spectra of oligomer **5, 6, 7** (left) and co-aggregates **1*5**, **1*6**, **1*7** in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 μM.

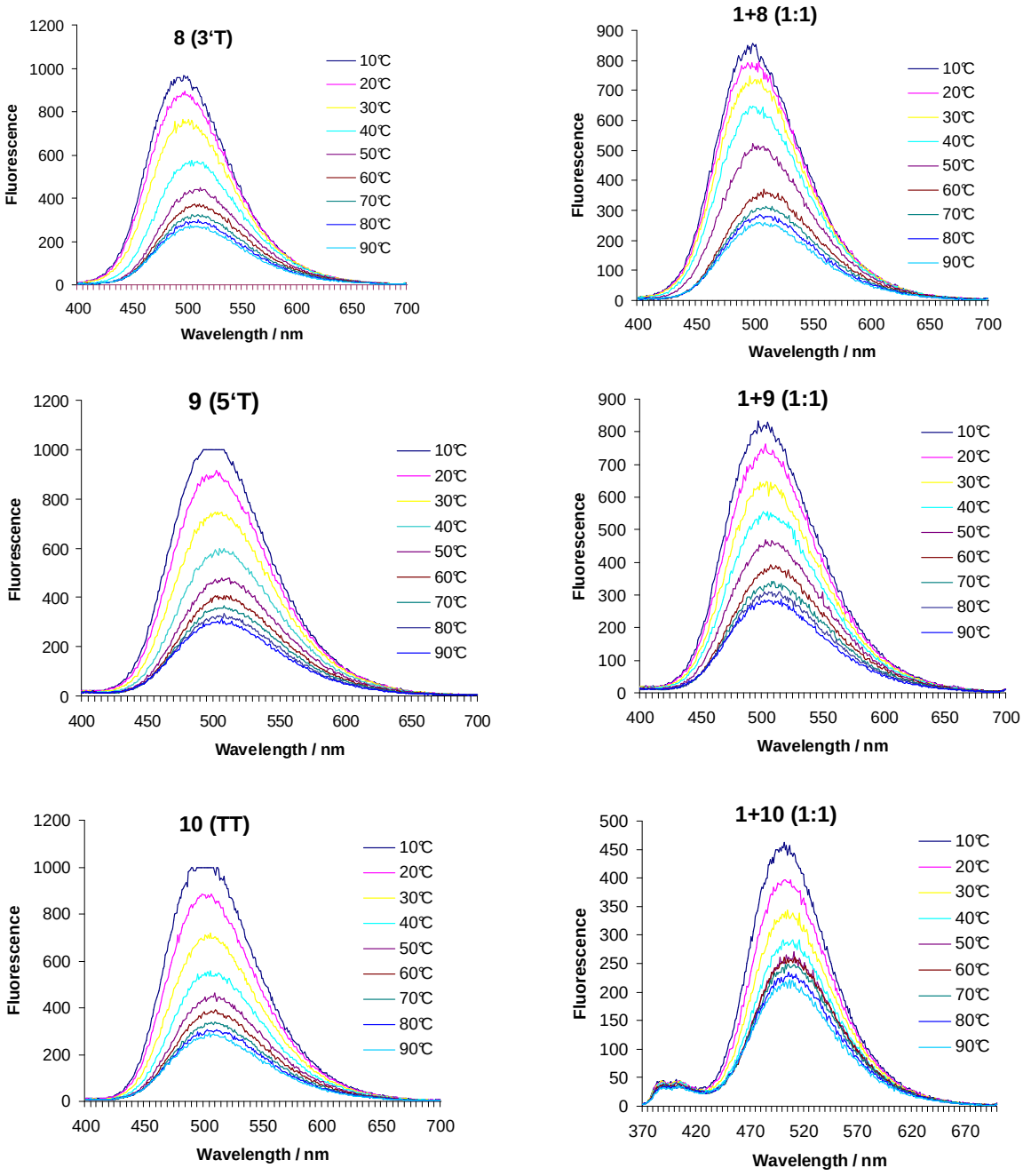

Figure 20. Temperature variable fluorescence spectra of oligomer **8, 9, 10** (left) and co-aggregates **1*8**, **1*9**, **1*10** in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 μM.

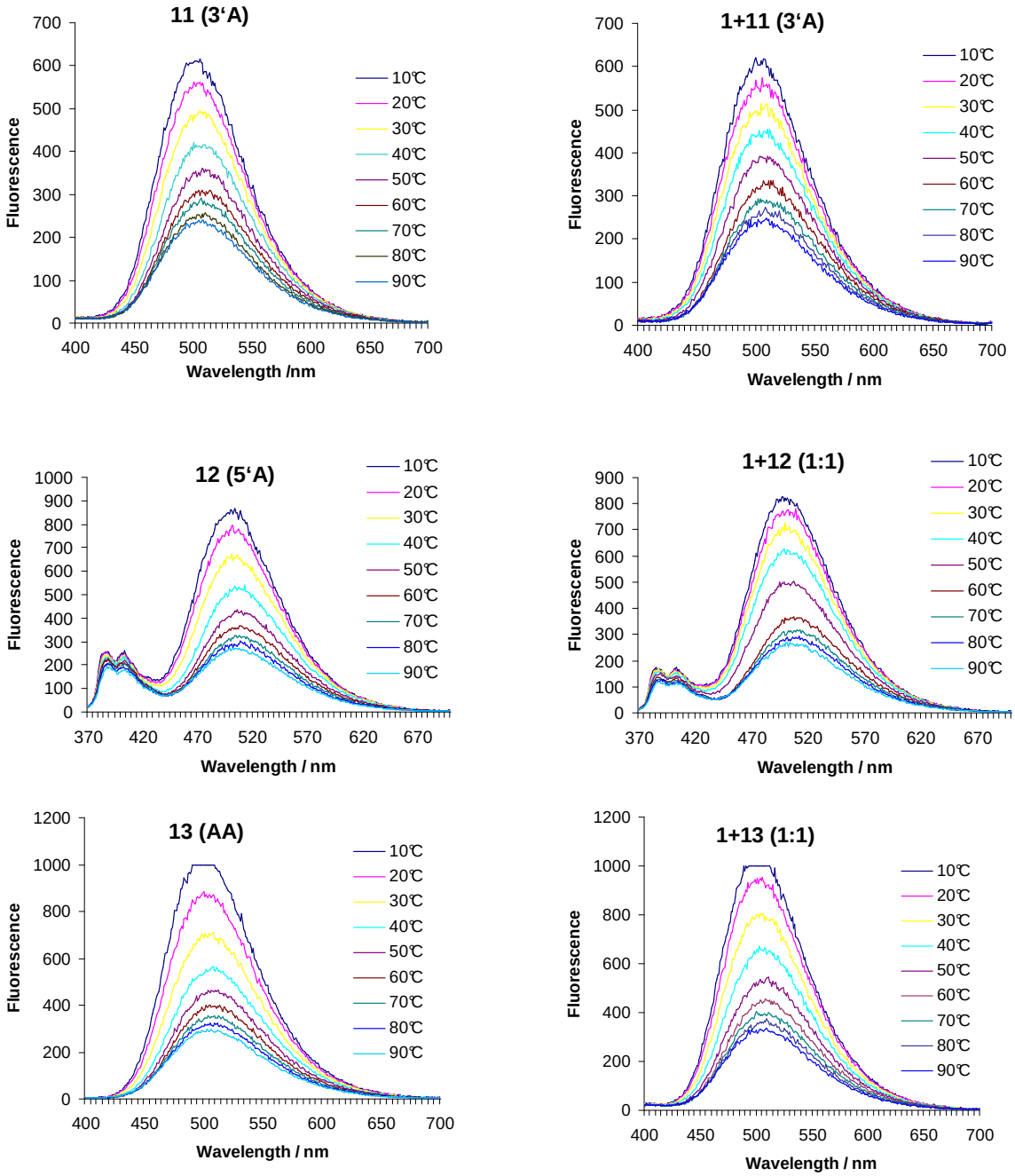

Figure 21. Temperature variable fluorescence spectra of oligomer **11, 12, 13** (left) and co-aggregates **1*11**, **1*12**, **1*13** in a 1:1 ratio (right). Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 μM.

The effect of nucleobase complementarity

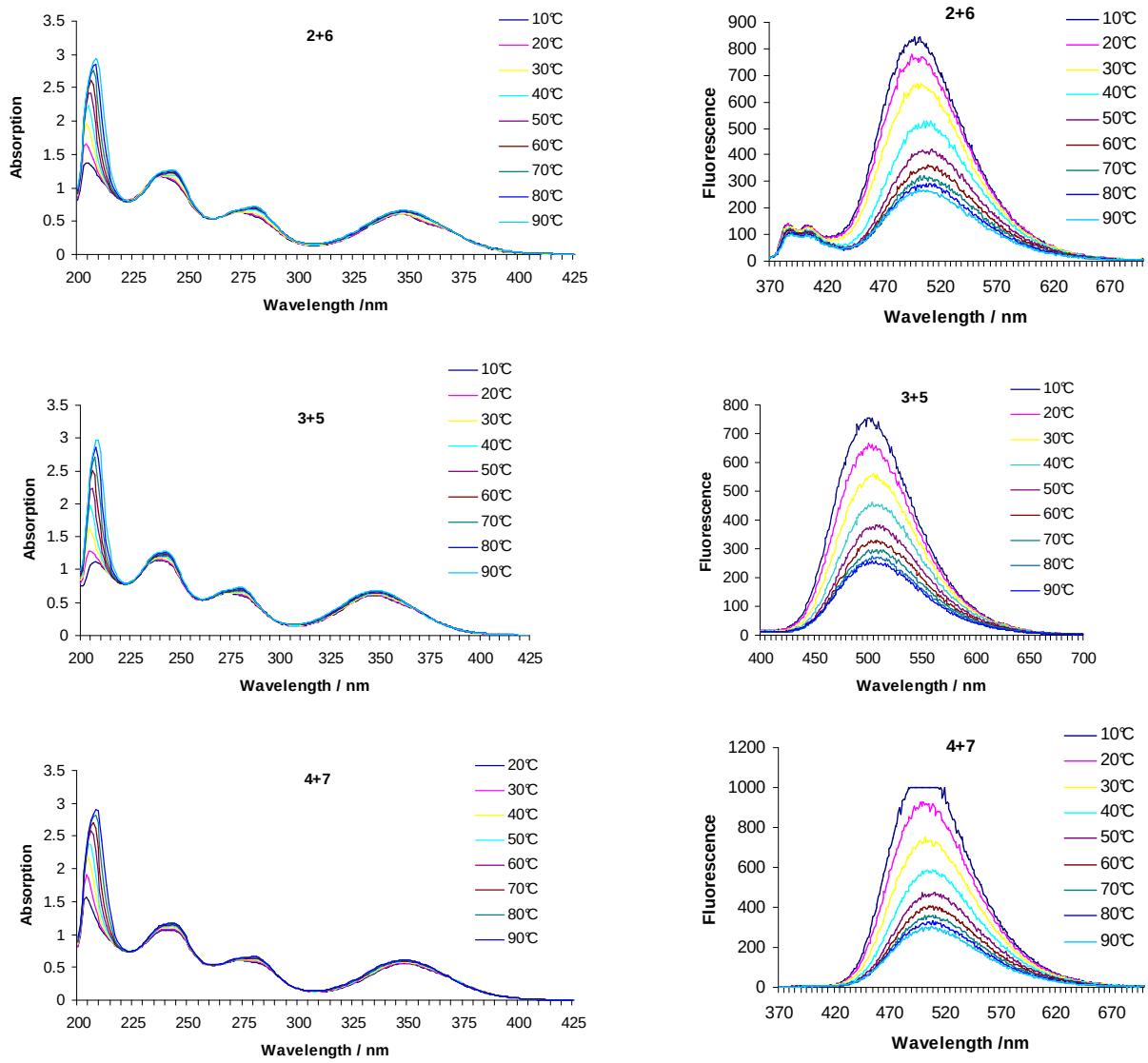

Figure 22. Temperature variable absorption spectra (left) and fluorescence spectra (right) of oligomer **2, 3, 4** and its complementary base. Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 μM.

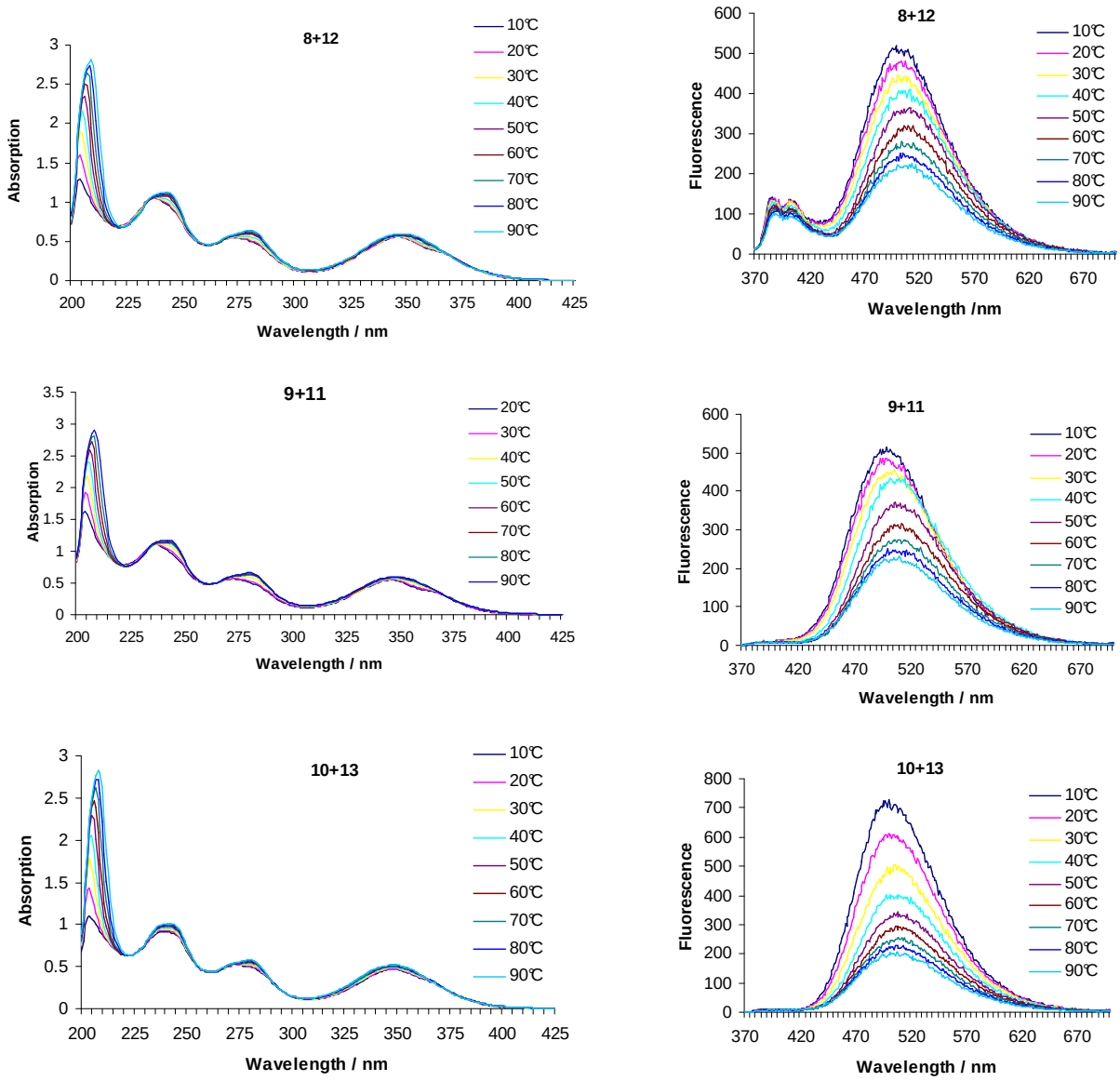

Figure 23. Temperature variable absorption spectra (left) and fluorescence spectra (right) of oligomer **8, 9, 10** and its complementary base. Conditions: sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 μM.

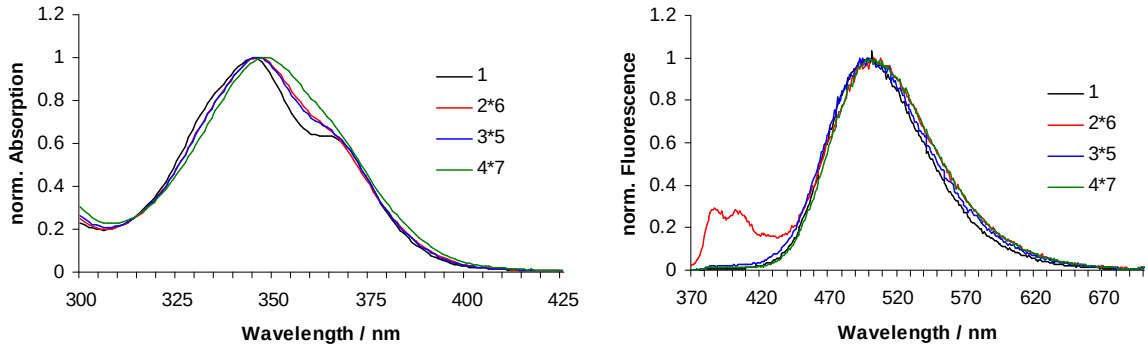

Figure 24. Normalized absorbance (left) and fluorescence (right) spectra of **2*6** (Py_7-C)* (G-Py_7), **3*5** (C-Py_7)* (Py_7-G), **4*7** (C-Py_7-C)* (G-Py_7-G). Conditions:sodium phosphate buffer, pH =7.0, 1 M NaCl. Total concentration of pyrenyl containing blocks: 5 µM.

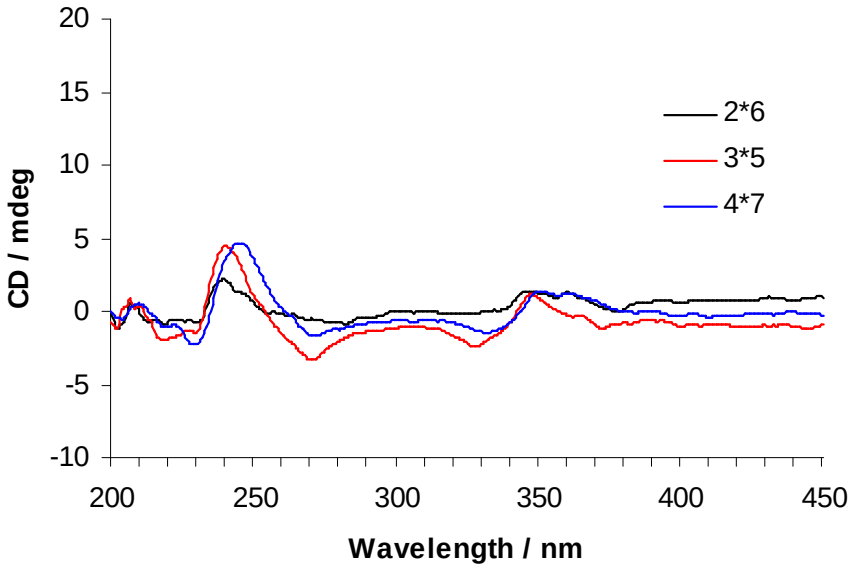

Figure 25. CD-spectra of **2*6** (Py_7-C)* (G-Py_7), **3*5** (C-Py_7)* (Py_7-G), **4*7** (C-Py_7-C)* (G-Py_7-G). Conditions: see Fig. 11.

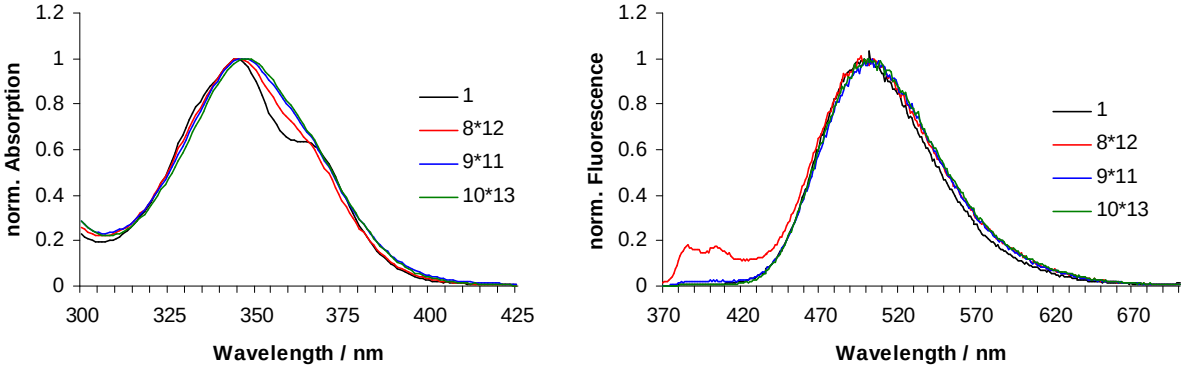

Figure 26. Normalized absorbance (left) and fluorescence spectra (right) of **8*12** (Py_7-T)* (A-Py_7), **9*11** (T-Py_7)* (Py_7-A), **10*13** (T-Py_7-T)* (A-Py_7-A). Conditions: see Fig. 11.

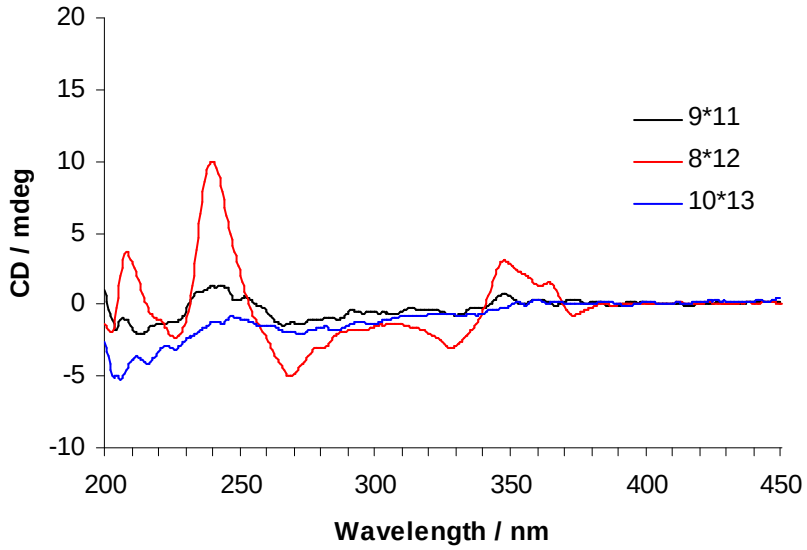

Figure 27. CD-spectra of pyrene oligomer **8*12** (Py_7-T)* (A-Py_7), **9*11** (T-Py_7)* (Py_7-A), **10*13** (T-Py_7-T)* (A-Py_7-A). Conditions: see Fig. 11.

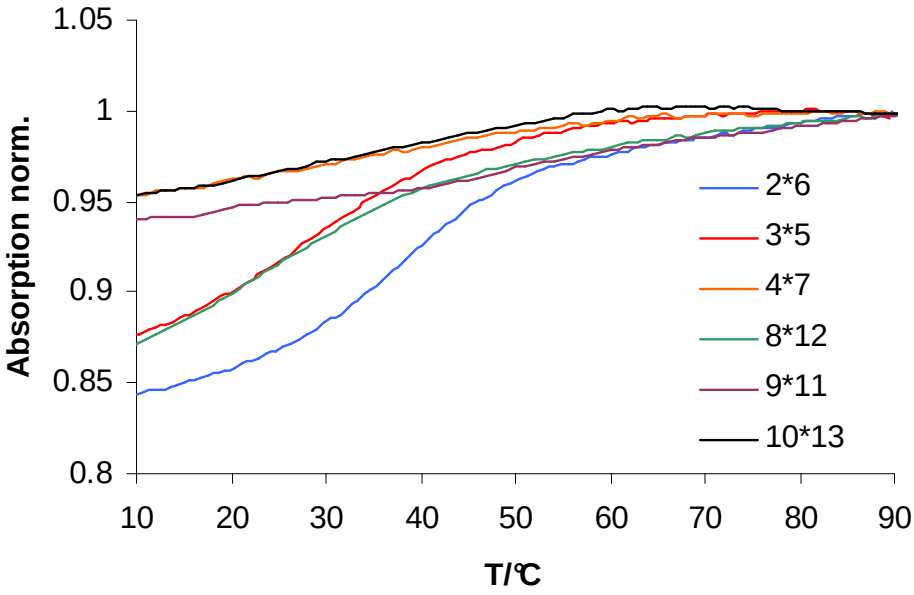

Figure 28. Melting profile of the co-aggregates **2*6**, **3*5**, **4*7**, **8*12**, **10*13** in a 1:1 ratio. Conditions: see Fig. 11.